### Robust and electrochemically active polymer-derived ceramic composites as electrodes for HER

Involved PNM researcher: Chrystelle Salameh, Philippe Miele, Damien Voiry

Hydrogen, the most environment-friendly fuel with the highest energy density, is considered more and more as an energy carrier for applications such as hydrogen cars and power stations. One way to produce hydrogen is via electrocatalytic water splitting, which still relies on the catalysts with superior activity. This imposes that the catalysts for the Hydrogen Evolution Reaction (HER) – the half reaction involved in water splitting – must be thermodynamically and kinetically optimized. As we know, Platinum is the best catalyst for the hydrogen evolution reaction, however it is scarce, unstable and very expensive, which limit its widespread use. Therefore, research recently was aiming to developing novel sustainable and affordable catalysts for the Hydrogen Evolution Reaction. Polymer-derived ceramics have been found recently to be eligible for electrochemistry applications for energy storage. We show for the first time the catalytic activity of polymer derived ceramics as electrodes for the hydrogen evolution reaction.

We developed a novel approach combining the polymer-derived ceramics approach with the hydrothermal synthesis of graphene oxide aerogels to produce composites with a great control of the chemical composition, structure, phase distribution and porosity. Modified-silicocarbonitride ceramics and the composites with graphene were found to be electrically conducting, mechanically strong and electrochemically active while demonstrating outstanding activity over several days under HER operation. Our results unveil the potential polymer derived ceramic for the hydrogen evolution reaction and open avenues for further exploration of the use of polymer derived ceramic graphene composites in electrocatalytic reactions.

Precursors chemistry: from synthesis to energy applications
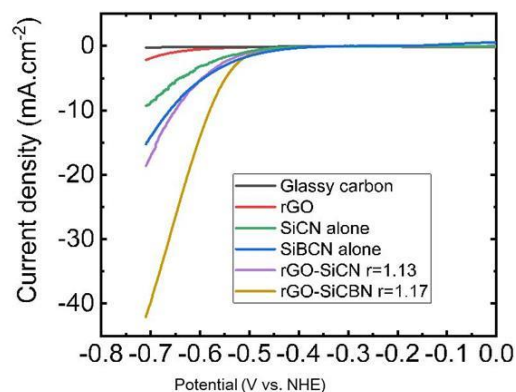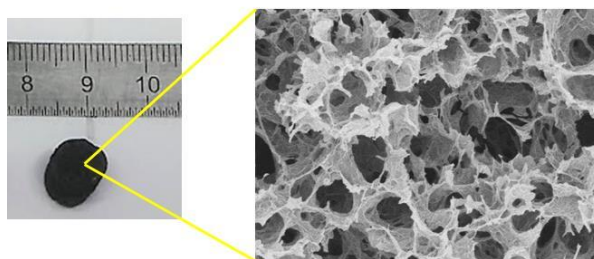
Porous nitrides with interconnected mesoporous network, high surface areas and pore volumes for hydrogen storage

Collaboration: A. Bruma (NIST, Maryland US)
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We synthesized mesoporous monolithic (3D) boron nitride (BN) structures by a template-assisted polymer-derived ceramic route. Polyborazylene was selected to impregnate monolithic activated carbon used as template. It supplies, after pyrolysis and template removal, BN components with controlled crystallinity and tunable textural properties according to the temperature at which they have been annealed (from 1000 to 1450 °C). Monoliths with an interconnected mesoporous network, high specific surface areas from 584 to 728 $m^2.g^{-1}$, significant pore volumes from 0.75 to 0.93 $cm^3.g^{-1}$ and a relatively high compressive strength are generated. Then, we used these highly porous compounds as nanoscaffolds to confine ammonia borane. The composites provided a remarkable effective gravimetric hydrogen capacity up to 8.1 wt%, based on AB measured at 100 °C, a value which demonstrates the high potential of our system as a safe potential hydrogen storage material. Considering the effective regenerability of AB, these results suggest that the BN-based composite material is a safe potential hydrogen storage material.
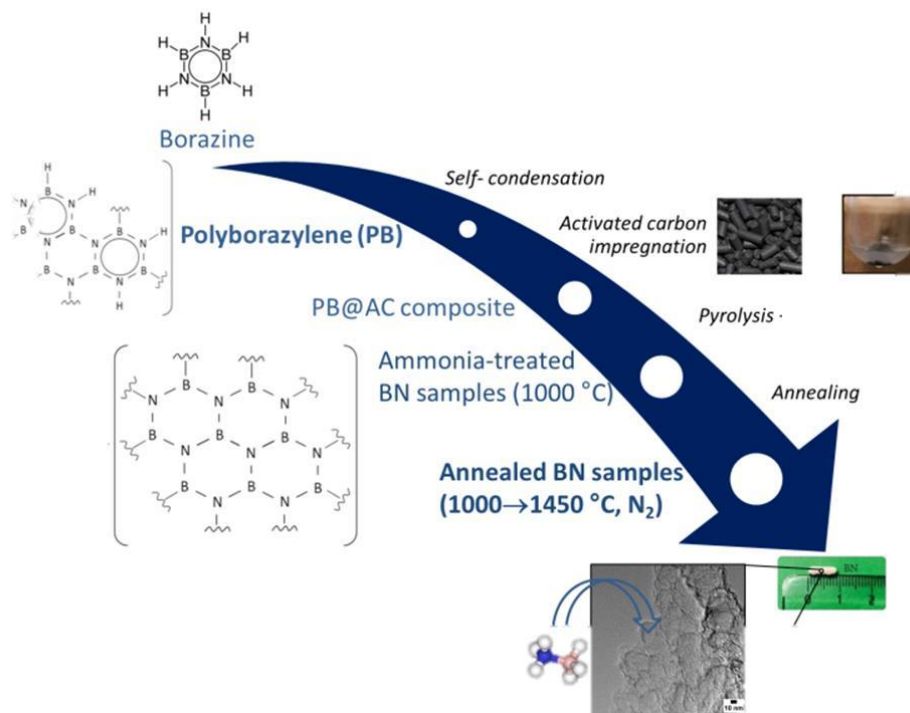
Porous nitrides with ordered (micro)mesoporosity, high surface areas and pore volumes as catalyst support for hydrogen production

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Late transition metal have attracted considerable interest for catalytic applications. Their immobilization over supports with tailored porosity is advantageous for nanosizing metal particles and avoiding their agglomeration which is known to bring a serious issue to the catalytic performance. Herein, ordered mesoporous silicon nitride (Si_3N_4) nanoblocks with hexagonal symmetry of the pores, high specific surface areas (772.4 $m^2\ g^{-1}$) and pore volume (1.19 $cm^3\ g^{-1}$) are synthesized by nanocasting using perhydropolysilazane as precursor. Then, Si_3N_4 nanoblocks are used as supports to synthesize platinum nanoparticles (Pt NPs) by precursor wet impregnation. Detailed characterizations by TEM show that monodispersed spherical Pt NPs with a 6.77 nm diameter are successfully loaded over nanoblocks togenerate nanocatalysts. The latter are subsequently used for the catalytic hydrolysis of sodium borohydride ($NaBH_4$). A hydrogen generation rate of 13.54 L min^{-1} gPt^{-1} is measured. It is notably higher than the catalytic hydrolysis using Pt/CMK-3 nanocatalysts (2.58 L min_1 gPt^{-1}) most probably due to the textural properties of the Si_3N_4 supports associated with the intrinsic properties of Si_3N_4. This leads to an attractive nanocatalyst in pursuit of practical implementation of B-/N-based chemical hydrides as a hydrogen source for fuel cell application.
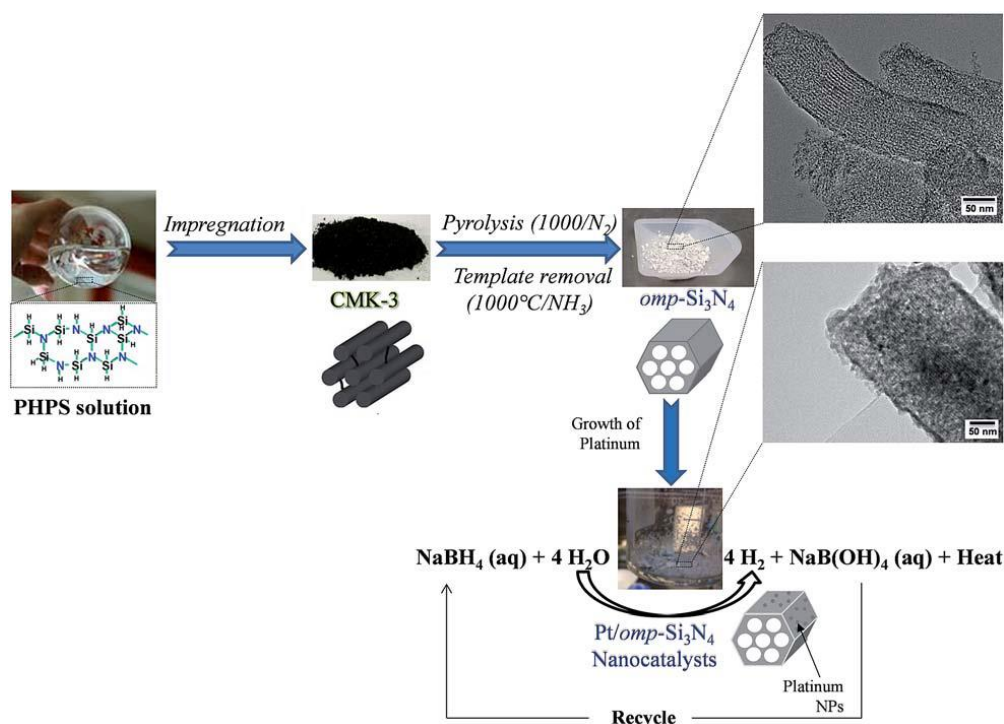
Tailor-made synthesis of boron- or aluminium-modified SiCN

A series of polyaluminosilazanes was synthesized by reaction of dimethylethylamine alane complex with polysilazanes. Starting from different dichlorosilanes, polysilazanes were obtained by means of ammonolysis. The latter reacted with the alane complex and led to solid polyalumino(carbo)silazanes that can be described as "custom-made" polymers since we monitored and controlled all the steps (from the choice of the molecular precursor to the polymerization and the functionalization with aluminum) in order to study the effect of the introduction of Al on the different reactive sites of the Si- backbone in the polysilazanes. Detailed information on the polymer structures were obtained by FTIR and multinuclear solid state NMR spectroscopies. The transition from the polymeric state to the ceramic inorganic state was investigated by means of solid-state NMR spectroscopy and finally the structural evolution of the final ceramics by high angle XRD, Raman spectroscopy and TEM imaging. It is noted that the polymer-derived SiAlCN ceramics are X-ray amorphous even at high temperature under nitrogen with some local crystallization. Upon further heating these materials tend to further crystallize into thermodynamically stable phases at a given chemical composition, such as SiC, Si_3N_4, free C, or AlN. Finally, the present study shows that the amorphous-to-crystalline transition is closely related to the nature and structure of the preceramic polymer.